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REVIEWS

Review

Progress toward Commercial Application of Electrochemical Carbon Dioxide Reduction

Chi Chen,[1] Juliet F. Khosrowabadi Kotyk,[1] and Stafford W. Sheehan[1,*]

Climate change is one of the greatest challenges facing humanity, and our continued sustainable development requires a portfolio of solutions to ultimately reduce the use of fossil fuels and decrease the concentration of carbon dioxide in our atmosphere. Chemistry is central to tackling this issue, and of the pathways to transform carbon dioxide into value-added compounds, single-step electrically driven chemical methods have attracted substantial interest in the last decade. This review places emphasis on the barriers that chemists must overcome to realize this technology and enable commercial use of electrochemical carbon dioxide reduction. We outline design strategies for gas-diffusion electrodes and electrolyzers that follow fundamental principles of catalysis to bridge the gap between catalyst discovery and integrated system engineering. These should address both technical (thermodynamic and kinetic) and practical (infrastructural) hurdles to implementation. We conclude by discussing how these approaches can be improved to help achieve a carbon-neutral economy.

INTRODUCTION

Increasing global carbon dioxide flux into Earth's atmosphere by fossil fuel combustion has not been balanced by an increase in the intensity of natural carbon sinks, causing a net increase in atmospheric greenhouse gas concentrations that affects global climate change, air quality, human health, and energy security.[1] The primary product of fossil fuel combustion is carbon dioxide (CO_2), which is emitted into the atmosphere from point sources, including fossil fuel-based power plants, as well as more distributed emitters such as automobiles and airplanes. In 2015, 36.2 billion metric tons of CO_2 was emitted to the atmosphere from anthropogenic sources,[2] corresponding to an increase in global mean temperature of around 0.1°C since then.[3] The economic impact of this is a cost burden that can total as high as $1.5 trillion between 2015 and 2050 when the aggregate harm to global agricultural productivity, human health, property damage, and energy systems is taken into account—the social cost of carbon.[4,5]

The critical need to counteract this atmospheric CO_2 increase has motivated researchers and entrepreneurs to develop processes that attenuate CO_2 emissions.[6] Low-cost methods, such as reforestation and soil amendment, hold promise for distributed carbon capture; however, their land and water requirements are not amenable to high-throughput CO_2 fixation. These should be supplemented by methods that convert CO_2 into economically viable compounds with high feedstock abundance.[7] Technologies that utilize CO_2 in this manner include algae-based biofuel production, carbonate fixation (e.g., novel curing methods for concrete),[8] and electrochemical conversion.[9] Climate scientists have noted that it is necessary to

The Bigger Picture

The increasing concentration of carbon dioxide in our atmosphere poses a threat to the environment and energy security as humanity's population grows. Taking action to preserve Earth's climate, which is the 13th UN Sustainable Development Goal, will require many different technologies that reduce both the carbon emissions of existing processes and those that efficiently utilize carbon dioxide as a feedstock for chemicals and fuels. Following this, key discoveries in the 20th century demonstrated the breadth of products that could be made electrochemically from carbon dioxide, including carbon monoxide, methanol, ethylene, and ethanol. Now, researchers must improve on this fundamental science to engineer practical and economic carbon dioxide electrolysis systems. This review highlights the progress that chemists have made and the barriers that must still be overcome before electrochemical carbon dioxide reduction technologies can be realized in industry.

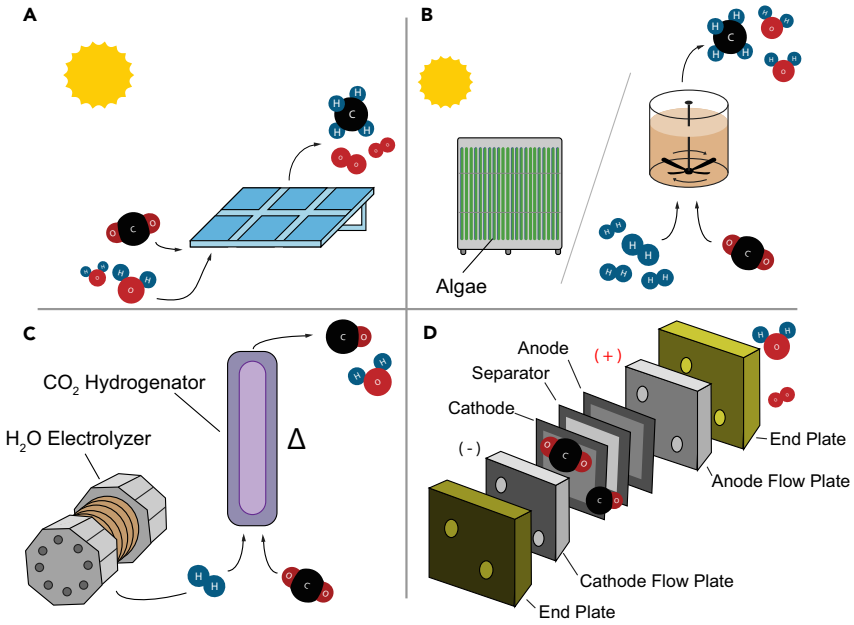

Figure 1. Carbon Dioxide Conversion Strategies

A schematic depicting selected (A) photochemical and photoelectrochemical, (B) biochemical, (C) thermochemical, and (D) electrochemical methods of producing syngas, alkanes, alcohols, or carboxylic acids from water and carbon dioxide.

adopt technologies that are carbon negative, similar to the ones described above, to have a >50% chance of meeting the international goal to limit modern global warming to $\Delta T_{global} < 2^{\circ}C$.[10]

Many low-cost methods of CO_2 sequestration, such as reforestation, use existing natural oxygenic photosynthetic processes to convert CO_2 into organic carbon using water as a source of protons and electrons, sunlight as a source of energy, and oxygen as a by-product.[11] Energy losses and rate limitations in natural photosynthesis, as well as a finite annual growth cycle in most climates, limit the efficiency and rate of these plant-based approaches for globally viable technology.[12] Nonetheless, nature has shown us that using water as a proton source and oxygen as a sole by-product is compatible with Earth's atmosphere and geochemistry on a global scale. We must now develop technologies capable of concentrating renewable energy and converting CO_2 more effectively than nature.

Technologies that use water and CO_2 to produce oxygen and an economically viable primary product, capable of being powered by renewable energy, can be divided into four different categories: (1) photochemical, (2) biochemical, (3) thermochemical, and (4) electrochemical and various hybrid approaches. Figure 1 shows examples of these pathways. Similar to photosynthetic processes, photochemical and photoelectrochemical conversion require solar energy capture cost-competitive with utility-scale silicon photovoltaics ($0.05/kWh levelized cost, $\eta \approx 20\%$)[13,14] and corresponding product collection over the same surface area,[15] which are both considerable challenges. Relevant electrically driven microbial approaches are multi-step and rely on electrolysis.[16,17] H_2 gas from water electrolysis can also be used to thermochemically hydrogenate CO_2 into a final product, yet this process suffers energy losses in H_2 compression, product separation, and yield.[18] Single-step electrochemical approaches that convert CO_2 and water directly into

[1]Catalytic Innovations, 151 Martine Street, Fall River, MA 02723, USA

*Correspondence: staff@catalytic-innovation.com

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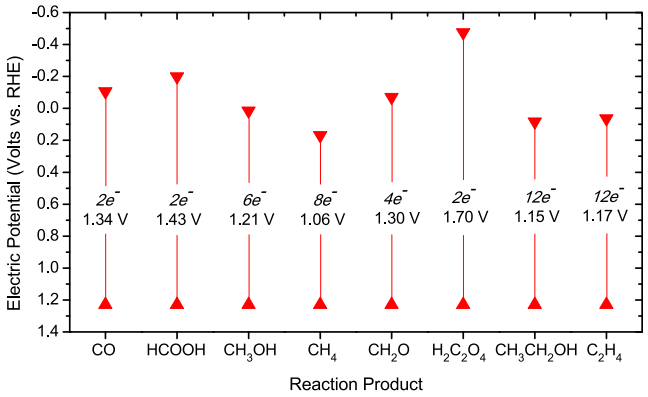

Figure 2. Standard Reduction Potentials for Small-Molecule Products

These are determined from CRC Handbook data[24] for selected common C_1 and C_2 products of CO_2 reduction: carbon monoxide, formic acid, methanol, methane, formaldehyde, oxalic acid, acetic acid, ethanol, and ethylene.

small-molecule products present an opportunity to prevent some of these losses by operating under milder conditions with higher selectivity, but have their own drawbacks centered around system stability and intolerance to feedstock impurities.[19,20]

Each strategy for CO_2 conversion has its unique economic advantages and must be included in the portfolio of solutions to reduce atmospheric CO_2 concentrations; thus we do not advocate any one method as superior to others. For example, a thermochemical approach may be ultimately favorable if there is underutilized hydrogen available, such as from a chlor-alkali facility. Photoelectrochemical approaches may be most useful for remote or isolated applications where rapid deployment provides value,[15] and electrolyzers are most economic when the cost of electricity is low. Still, after technological development for decades, no commercialization in any of these categories has yet been realized. This is due, in part, to the low cost and abundance of feedstock materials made from fossil fuels.

The goal of these CO_2 utilization technologies is very ambitious: to disrupt a $5 trillion dollar market[21,22] by producing fuel and commodity chemicals at a price point lower than petrochemicals can afford, while maintaining environmental sustainability. Pathways toward reaching that goal begin in less conservative markets that can more rapidly develop infrastructure for new technologies.[23] In this review, we highlight studies that address the barriers to scalable and practical implementation of electrochemical CO_2 reduction in this manner.

CO_2 ELECTROLYSIS

We define a CO_2 electrolyzer as a device that uses electricity to convert CO_2 into reduced carbon-containing products. In a manner akin to photosynthesis, charge balance is provided by protons and electrons, which are produced by oxidizing water to by-produce O_2. This process, in turn, forms a proton gradient in the electrolyte connecting anode and cathode, as protons are consumed by cathodic CO_2 reduction and generated by anodic O_2 generation. This chemistry is driven by an external applied voltage, which provides high-potential electrons capable of reducing CO_2 at the cathode, to make small molecules such as carbon monoxide ($E^o_{CO_{(g)}} = -0.11\ V$ versus RHE), formic acid ($E^o_{HCOOH_{(aq)}} = -0.20\ V$ versus RHE), and many others, as shown in Figure 2. The externally produced electric energy is thus stored as chemical energy in the desired product.

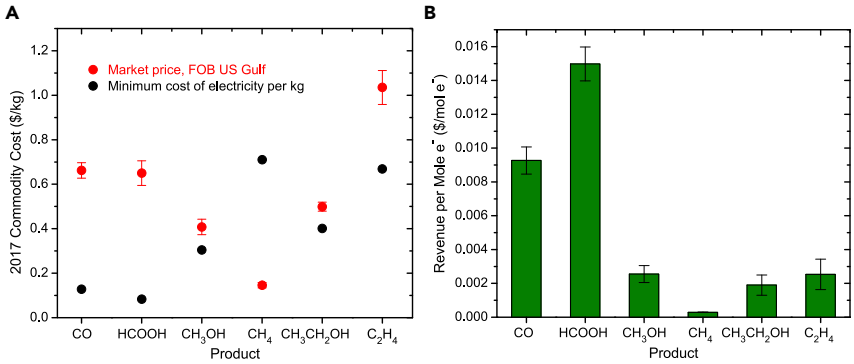

Figure 3. Economic Analysis for Five CO_2 Electrolysis Products in Large Commodity Markets

(A) 2017 US commodity price at its highest-volume purity compared with the cost of electricity for the formation of carbon monoxide,[27–29] formic acid,[30] methanol,[31] methane,[32] ethanol,[26] and ethylene[33] at their reversible potentials (assuming $0.05/kWh).

(B) The value generated per mole of electrons consumed for each. For each case, additional risk factors based on market fluctuation, transportation cost, capital cost, and purification must also be taken into consideration.

For this to become a viable way to produce these products on a global scale in the long term, three different types of limitations must be understood and confronted: (1) thermodynamics, (2) kinetics, and (3) infrastructure, such as process design and integration with existing low-cost CO_2 input streams. Decreasing global electricity costs compared with the prices of small-molecule commodity chemicals improves the value proposition for CO_2 electrolysis. For example, fuel ethanol is a large global commodity with 78.9 Mt $year^{-1}$ produced annually using fossil fuel-derived feedstocks, and a 2017 average $0.39/L free on board (FOB) price on the US Gulf Coast, inclusive of all subsidies.[25,26] Electrochemical ethanol production from CO_2 is a 12-electron process with $E^{o}_{Ethanol}$ = 0.084 V versus *RHE*. If a $0.05/kWh cost of industrial electricity is assumed, one can calculate the minimum cost of ethanol produced by renewable CO_2 electrolysis as $0.32/L. A minimum thermodynamic electricity cost, such as this, is representative of the revenue a product can generate per kWh of electricity consumed. Still, it must be seen as a starting point rather than a quantitative measure, since accessing ethanol may require higher-energy reaction intermediates, such as CO.

Similar analysis comparing other single-step CO_2 reduction reaction products with their 2017 commodity price can be seen in Figure 3A. For a quantitative measure that is independent of electricity cost, kinetics, and thermodynamic potentials of intermediates, these reactions can be can be benchmarked by comparing price with the number of electrons it takes to make each product, shown in Figure 3B. This tells us how much economic value can be generated per mole of electrons, and when adjusted by electrolyzer cell potential can be used to maximize revenue in applications where the cost of electricity is negligible, such as electrical grid load leveling. While this figure of merit uses average 2017 US Gulf Coast FOB prices as a standard, these values are frequently higher around the globe depending on supply, demand, subsidy, market volatility, and transport costs.

Kinetic and infrastructural costs must then be factored in and contrasted with the benefits of electrolysis, e.g., on-site production and product purity. For more favorable thermodynamics, there is also important applied research and development on processes that use proton and electron sources other than water.[34,35] The oxidative half-reaction in these processes use C–H bond oxidation reactions in waste or other

low-cost feedstock, which provide protons and electrons with a lower thermodynamic energy cost than water oxidation. There is also the potential to utilize electrons from reactions in the existing electrochemical industry that generate economically useful oxidation products, such as the chlor-alkali process for Cl_2 production.

At this point, our understanding of thermodynamics is sufficient to demonstrate that it is possible for CO_2 electrolysis to be cost competitive in a variety of global markets. Technology development must now play a role in addressing catalytic (kinetic overpotential, selectivity, and stability) and other practical (ohmic losses in the cell, product separation, and infrastructure for CO_2 capture) barriers. CO_2 electrolysis faces the need for a high level of infrastructural overhaul, as well as high-onset capital expenses. This overhaul brings with it a higher risk of going from proof-of-concept to pilot production, both of which are a major factor in its slow commercial uptake. Other obstacles, such as energy policy and subsidies in place for incumbent industries, cannot be immediately addressed by scientific research and development. In the long term, however, scaled and functional technologies will frame a better case for implementation of such policies for CO_2 electrolysis.

TECHNOLOGICAL CHALLENGES

The first practical challenge for any CO_2 conversion technology is determining how best to source CO_2 because reconciling the cost of CO_2 capture is a substantial hurdle. Pure CO_2 is a commodity itself, with historical prices as high as $26 per ton, and has many uses in industry today.[36] Therefore, high-volume waste CO_2 must be utilized if commodity or fuel markets are ultimately desired. This requirement limits practical CO_2 sources to industrial outputs such as steel and cement production, power plant flue gas, or the atmosphere.

Direct air capture from atmosphere, while not currently a widespread, economically viable method of capturing pure CO_2, becomes gradually less costly and energy intensive as lower concentrations of output CO_2 in air can be tolerated by a connected CO_2 conversion technology. Conventional physical adsorbents for air capture require only modest energy inputs, around 0.34 kWh/kg_{CO2} for CO_2 desorption.[37] The cost of compressors and peripheral systems for desorption to occur in a vacuum greatly increase system costs; thus, methods for selective conversion of CO_2 at moderate concentrations in air are advantageous from an economic perspective.

Technology that can operate with CO_2 concentrations between 5% and 12% access both reduced air-capture cost, as well as the potential to utilize a flue gas feed from natural gas-fired power plants. Coal-fired power plants provide even higher concentrations of CO_2 in flue gas, but come with more impurities such as SO_x, NO_x, and particulates.[38] In both flue gases, O_2 is present at considerable concentrations, which introduces the oxygen reduction reaction as a side reaction. Despite feedstock CO_2 concentration and purity being a major practical barrier to implementation, there is a gap in our understanding of catalyst and membrane deactivation, selectivity for CO_2 in O_2-, N_2-, and impurity-containing reactant streams, methods of reducing CO_2 present in capture solvents,[39] and the effect of increasing CO_2 concentration at catalyst surfaces by physical (high-pressure) or chemical methods.[40,41]

The majority of CO_2 electrolysis research and literature strives to address barriers surmountable by electrocatalyst optimization: (1) overpotential, (2) selectivity or faradic efficiency, which is the percentage of electric charge that is used for formation of the desired product, (3) sustained catalytic current density and, most critical

for early-stage technologies, (4) stability. Of these, product selectivity presents a notable competitive advantage over other technologies. Three decades ago, Hori and coworkers showed that a wide breadth of products, including methane and ethylene, can be synthesized electrochemically in a single-step reaction from CO_2 with copper catalysts.[42,43] These seminal works are important because they show that multiple useful feedstock chemicals can be made by CO_2 electrolysis, rather than only C_1 products that had been demonstrated decades before.[44,45] Over 16 simultaneous products have been detected from CO_2 reduction electrolysis,[46] and reports of faradic efficiencies near to 100% are not uncommon for CO and formate (HCOOH).[47–49] High faradic efficiencies allow for tailored production of chemicals with the potential to reduce the cost of product separation, for example, lowering the energy required in distillation processes that account for as high as 50% the cost of production for products such as ethanol.[50,51]

In addition to CO and HCOOH, many studies have focused on formaldehyde (HCHO), methanol (CH_3OH), methane (CH_4), oxalic acid ($H_2C_2O_4$), ethylene (C_2H_4), and ethanol (CH_3CH_2OH) as CO_2 electrolysis products. Electrolysis systems that make these must be capable of producing substantial mass of the desired product (m_p) over a short time (t) and across small electrode surface areas (A) to keep capital costs low. This balance is achieved by sustaining a high yield, represented by faradic efficiency (η_{FE}) and reaction rate, which is related to current density (J) by Faraday's law, which states that the amount of chemical reaction caused by current flow is proportional to the amount of electricity passed through the electrode,[52]

$$m_p = \frac{M_p JAt}{nF}\eta_{FE},$$

where n is the number of electrons that must be transferred to form one molecule of the desired product, and M is the molar mass of the desired product.

For practical CO_2 electrolysis, current densities of 100–1,000 mA cm^{-2} are highly preferable, but CO_2 has low solubility in aqueous conditions, which limits many laboratory-scale cases to be on the order of 1–10 mA cm^{-2}. Aqueous solvents also enable the parasitic hydrogen evolution reaction (HER), which diverts protons away from CO_2 reduction.[53] Low pH favors hydrogen production and high temperatures reduce CO_2 solubility; therefore, many CO_2 electrolyzers operate at room temperature (25°C) and standard pressure (1 atm) with CO_2-saturated aqueous alkaline solutions containing alkali hydroxides or carbonates.[53] CO_2 equilibrates in water to form carbonic acid, altering the pH levels to more acidic values in some systems that use high pressure to increase solution CO_2 concentrations.[54] However, elevated pressures of CO_2 also disfavor the HER and shift product selectivity to higher-order carbon products.[55–57]

Fuel and large-scale commodity markets are beneficial to show the long-term potential of CO_2 electrolysis technologies. However, realistic commercialization in the next 10–20 years will be in smaller markets that are receptive to new technologies, especially ones that do not directly compete with low-cost fossil fuels.[58] While this technology's use is often cited as production of liquid fuels,[47,53,59–67] these markets are difficult to break into with heavily invested incumbent technologies. It is, therefore, more advantageous to focus on applications that emphasize the unique value propositions of CO_2 electrolysis. The ability to quickly achieve high current densities is desirable for leveling renewable energy output, grid frequency stabilization, and rapid on-site product generation. High selectivity allows for lower impurity concentrations in output streams, which is most valuable in chemical and consumer industries outside fuel.

In these decades before we reach the point where CO_2 electrolysis will disrupt gasoline markets, improvements to voltage efficiency beyond currently attainable values do not give a unique cost advantage over incumbent technologies that utilize low-cost fossil fuels. As such, while catalyst overpotential may be a major hurdle decades in the future, improving it does not address contemporary market pain points. Figure 3A shows that CO and HCOOH can absorb energy costs over triple their thermodynamic minimum if reliable and selective production is achieved with reasonable capital costs. It is, thus, critical to benchmark and understand how to control stability and selectivity in order to improve the design of both electrolyzers and catalysts around addressing these barriers.

CO_2 REDUCTION REACTION PRODUCTS

For heterogeneous catalysts that are most widely researched, in most proposed mechanisms the origin of the product made by CO_2 electrolysis begins with reduction of the electrophilic CO_2 molecule at a metal catalyst surface site (where * denotes a surface site or adsorbed species).[68] In the reduction mechanisms proposed by Hori, electron transfer to form a radical anion ($*CO_2^{\bullet -}$) is proposed as a first step in electrochemical CO_2 reduction.[55,68] There are also mechanisms whereby charged radical species are not proposed as an intermediate with the formation of a surface-bound *COOH by proton-coupled electron transfer as a first catalytic step.[69–73] Studies to elucidate a comprehensive understanding of these mechanisms are ongoing.

In most cases, metal catalysts have been delineated based on their reaction products, which is hypothesized to be representative of the bond strength between the catalyst metal and CO_2.[19,49,68,74] In this scheme, metals such as Au, Ag, Zn, and Ga usually form a surface bond with CO_2, facilitating inner-sphere electron transfer to cleave a $C–O^-$ bond and selectively produce CO. Other metals, including Pb, Hg, Sn, and Tl, do not strongly coordinate with CO_2, suggesting an outer-sphere electron-transfer mechanism. A charged CO_2-bound surface species would be sensitive to the concentration of protons, carbonate anions, and other charged species in solution, but adsorption geometry of such a species has not yet been observed experimentally.[75]

Catalysts and electrolyzers for CO and carboxylic acids are discussed below. These two target products are closest to commercial deployment because of their kinetic accessibility. CO_2 electrolyzers and reduction catalysts for the production of alcohols and alkenes have also received considerable attention and are briefly outlined. These have begun to show durability and economic feasibility required for commercial deployment. After these products, alkanes such as methane and ethane; and aldehydes, such as formaldehyde, are also viable, with research focused on understanding catalytic processes and materials.[47,53,59,61,62]

Carbon Monoxide and Syngas

As a two-electron, two-proton process this reaction proceeds in a kinetically accessible manner using simple metal catalysts, and as a result CO_2 electrolyzers that produce CO are the closest to commercialization of all products. Included in this category is synthesis gas (syngas), an industrial gaseous feedstock containing a 2:1 ratio of CO and H_2 that can be used to produce numerous commodity chemicals.[76] Whereas CO_2 binds strongly to metals such as Au and Ag, the uncharged surface-bound CO is not reactive with the metal surface and has an endothermic binding energy, which enables it to leave without being reduced further.

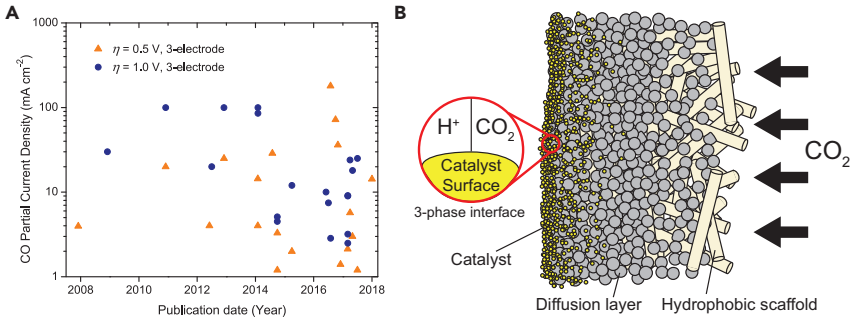

Figure 4. CO and HCOOH Production from CO_2

(A) Chronological trend in current density for CO production (>1 mA cm^{-2}) in peer-reviewed literature, as measured at atmospheric pressure in three-electrode configurations.[77–100]

(B) An example of gas-diffusion electrode architecture as described previously[104–109] depicts one configuration for catalyst incorporation into an electrolyzer producing CO or HCOOH.

Cathodes for CO production have reported catalytic current densities as high as 3.0 A cm^{-2} at high pressure,[41] and reports of catalysts capable of sustaining CO_2 reduction current densities in the tens to hundreds of mA cm^{-2} at moderate potentials under ambient conditions are increasing (Figure 4A).[77–102] These rates of production coupled with high faradic efficiency (>95%) suffice for many proposed commercial applications in beachhead markets. Electrolyzer stability in commercially relevant continuous-flow systems is demonstrated in two promising studies, with one noting 1,000 hr of operation,[103] and a more recent example achieving stability in a continuous closed-loop electrolyte system for over 1,200 hr.[17]

In most of these systems, catalysts are incorporated into electrolyzers on a gas-diffusion electrode (GDE) (Figure 4B), which allows direct contact between gaseous CO_2, the catalyst, and a liquid or polymer electrolyte. This enables rapid delivery of CO_2 to the catalyst, resulting in higher partial current densities by minimizing mass transfer limitations and circumventing the slow uptake of CO_2 in most electrolytes.[104–109] Other methods include using highly basic aromatic diamine "proton sponges" to increase solution CO_2 capacity, further enabling high reaction rates and HER suppression.[110] The most straightforward way to increase CO_2 delivery and partial pressure at the cathode is to pressurize the entire system, at the expense of increased capital costs. In one example, a continuous-flow system with a modified off-the-shelf electrolyzer used a 0.5 M K_2SO_4 catholyte and Ag catalyst at pressures above 15 atm to yield current densities as high as 350 mA cm^{-2} with 92% faradic efficiency for CO production.[111]

Primary barriers to implementation of these systems are practical and infrastructural, since they appear to be reliable and capable of high-rate production. Most continuous-flow CO_2 electrolyzers described here for CO production need pure CO_2 inputs, which is costly. In systems that achieve commercially relevant rates and durability, the catalytically active species is Ag metal. Understanding how to modify this component to allow selective coordination of CO_2 in dilute streams is a potential area for further study, understanding, and improvement.

Carboxylic Acids

After CO, HCOOH is currently the second most kinetically accessible product that can be made by CO_2 electrolysis. Mechanistic pathways have been proposed for HCOOH, an overall two-electron, two-proton process, for metals such as Sn and Pb that proceed with a lower affinity for CO_2. In these, CO_2 only weakly adsorbs

on these surfaces, accepting a proton and electron without C–O bond cleavage to form the free formate ($HCOO^-$) anion.[49,112] Computational studies suggest that pH control and catalyst alloying can allow for production of HCOOH with high rate and selectivity, and faradic efficiencies >90% have been reported at high current densities.[53]

To demonstrate the importance of pH control for formate production, using a continuous-flow microfluidic reactor with two separate catholyte and anolyte feeds for pH control, researchers have been able to achieve current densities as high as 345 mA cm^{-2} with a faradic efficiency approaching 95% and voltage efficiency near 50% for over 8 hr.[113] Many of these electrolyzers use organic solvents to control the pH dependence of formate production.[114,115] Beyond HCOOH, $H_2C_2O_4$ is a useful compound typically formed in non-aqueous solvents and is a potential intermediate to form other C_2 products.[116,117] Commercial development of a CO_2 electrolyzer or $H_2C_2O_4$ production using H_2 as a proton source has been performed with high faradic yields of >75% sustaining cell currents >7 A.[118]

Alcohols and Alkenes

After CO, HCOOH, and $H_2C_2O_4$, techniques that produce methanol, ethanol, and ethylene are approaching viability to produce a minimum viable product after decades of development.[119] Electrolytic production of saturated straight-chain alcohols requires six protons and six electrons per carbon by

$$nCO_2 + (6n)H^+ + (6n)e^- \rightarrow C_nH_{2n+1}OH + (2n-1)H_2O.$$

Methanol-selective production occurs on Ru and Cu.[49] These possess surface sites that form M–*CO_2 and M–*CO bonds while maintaining a sufficiently labile *CO species to further reduce to CH_3OH.[120] Functional GDEs have been made for methanol production with catalysts based on CuZn, a notable alloy that is also used as a commercial CO_2 hydrogenation catalyst for methanol synthesis, and have shown >20 hr of continuous operation.[108]

Formation of ethanol has sparked significant recent interest since its initial report decades ago.[43] While not a direct route from CO_2, studies of ethanol production from CO show how drastically synthetic conditions and intrinsic properties of the metal catalyst affect selectivity,[121] and following this logic, selectivity has further increased in recent years.[122–127] Ethylene also holds promise as a potentially high-value commodity, and reports of high faradic efficiency under sustained applied potential have been demonstrated.[58] A key next step for ethanol and ethylene systems will be understanding pH and CO_2 concentration control at GDEs to enable sustained partial current density >100 mA cm^{-2} across the electrode. Under these conditions, high pH has been shown to favor ethylene production with remarkable stability for over 150 hr,[128] while selectivity for ethanol has been improved in similar systems by engineering copper catalyst surfaces.[129]

ELECTROLYZER DESIGN

Selecting a target product helps to make the best economic case for a CO_2 electrolyzer, but electrolyzer design is of utmost importance—more so than for H_2 generation by water splitting. Small changes in the reaction environment (temperature, pressure, space velocity, ion availability, contaminants, and pH) prompt significant changes in reaction selectivity in CO_2 electrolyzers. The electricity, heat, water, and resources required to sustain a CO_2 electrolyzer affect scalability and practicality of these systems in different environments. It is further useful to benchmark systems on the basis of their feedstock requirements given that the economics for an electrolyzer that removes CO_2

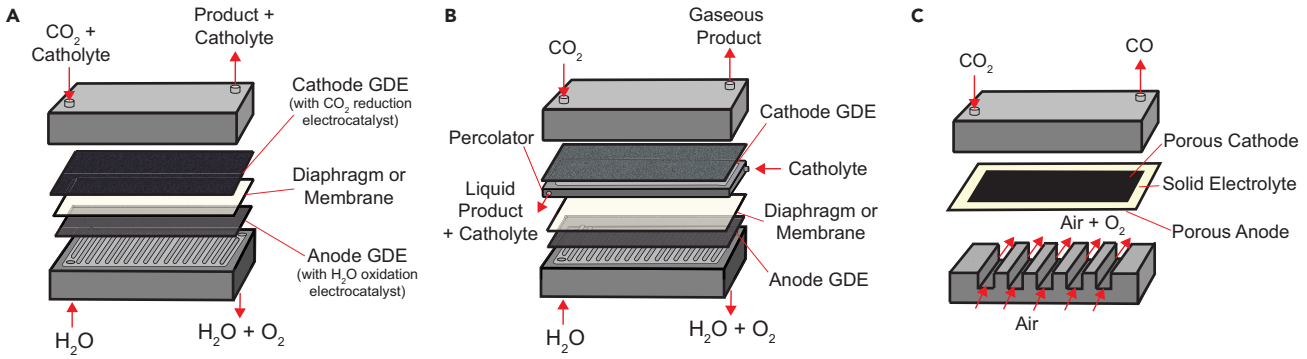

Figure 5. Examples of Continuous-Flow CO_2 Electrolyzers

(A) Type 1, which uses a liquid feed to the cathode where CO_2 is either dissolved or in ionic form.

(B) Type 2, which uses a gaseous CO_2 feed to the cathode while the anode is immersed in water, with either side being separated by a membrane or diaphragm.

(C) Type 3, which uses gaseous inputs to both anode and cathode; predominantly high-temperature solid-oxide electrolyzers. In these cases, electrical contact is made with the electrodes through the gray flow plates. In these diagrams, endplates, gaskets, charge collectors, and bolting are omitted for simplicity. GDE, gas-diffusion electrode.

from a capture solution are vastly different compared with one that requires a pure gaseous feedstock. Figure 5 shows examples from three classifications, developed to encompass all types of CO_2 electrolyzers based on feedstock requirements, to simplify the wide variety of reactor architectures that have been proposed. Critical to the function of these electrolyzers is their cathode GDE construction and properties, where reactants are introduced to catalyst metals.

Type 1: Dissolved CO_2 Catholyte

Electrolyzers that operate with both a liquid anolyte and catholyte, and require that CO_2 be dissolved in the catholyte, fall into this category. These systems use neutral aqueous, alkaline, or non-aqueous electrolytes, and ion conduction between anode and cathode frequently occurs through a liquid electrolyte. These systems are similar in construction to water-splitting electrolyzers and may or may not include a polymer electrolyte membrane (PEM) or diaphragm, yet all use cathode materials more selective for CO_2 reduction than platinum, as is found in electrochemical hydrogen generators.

These liquid electrolyzers allow for simple organic compounds to be used as electrocatalysts[130,131] and ionic liquids to be added to solution that allow higher utilization and residence times for the catalyst.[132,133] However, in the latter case, ionic liquids have been demonstrated to be unstable under the high current density conditions required for commercial systems.[134] Liquid electrolyzers also allow for direct reduction of CO_2 in a capture solution and solution tunability for pH and CO_2 capacity control with organic additives, which is a key area of study for applied systems.[39,110,135,136]

In type 1 electrolyzers, cathode GDEs are limited by CO_2 flux to the catalyst, which is a key metric for quantification in these systems when compared with type 2 and type 3 systems. In addition to catholyte CO_2 capacity, bubble formation must be taken into account when designing type 1 GDEs, and can be improved by low-cost solution additives such as propylene glycol.[137] Electrodes in these systems can be grown on planar substrates,[138] which gives more control of surface roughness[139] than type 2 GDEs that typically require dispersion on a scaffold. Critical figures when benchmarking these electrolyzers will be CO_2 capacity of the catholyte, additives that enable utilization of dilute CO_2 feeds, corrosion rate of the GDE, and ease of product separation. Standards for quantitative benchmarking of catalysts in these systems

have been proposed,[140] although quantitative comparison specific to GDEs between type 1 and 2 systems remains a challenge.

Type 2: Gas-Fed Cathode

This category is primarily PEM electrolyzers that use a dry concentrated CO_2 feed to a cathode incorporated into a gas-diffusion layer, with concomitant water feed to the anode, and have seen considerable success thus far toward building durable and stable systems. The defining feature of this type of CO_2 electrolyzer is that CO_2 reduction occurs at a triple point where CO_2 gas, the electrolyte, and catalyst are in simultaneous contact (see Figure 4B). The pH and surface acidity or basicity of the membrane play a large role in improving the yield of certain CO_2 reduction products. For this reason, many electrolyzers in this class maintain electrolyte on either side of the membrane or diaphragm, with a porous metal electrode in early examples,[141] or a GDE separating the liquid electrolyte from the CO_2 gas feed. Modern designs use hydrophobic materials, such as polytetrafluoroethylene (PTFE), as a scaffold material to improve gaseous CO_2 delivery to the catalyst.

A key development for many CO_2 PEM electrolyzers is the use of an anion exchange membrane, rather than a cation exchange membrane, which was first incorporated into a standard PEM electrolyzer used for water splitting modified with a cathode feed of CO_2 gas, resulting in to CO production with nearly 90% faradic efficiency.[142] Anion exchange membranes were used with some success and have led to numerous other products, leading researchers to investigate membrane-catalyst interactions in cells like these. A critical parameter in CO_2 electrolysis is local pH at the catalyst surface, and the pH at the surface of the nearby membrane is largely dictated by the membrane material used,[143] as well as electrolyzer architecture, to control porosity and kinetics in diffusion layers.[144]

GDE construction is particularly crucial for type 2 electrolyzers, as the cathode GDE separates a gaseous CO_2 feed from a liquid catholyte and enables simultaneous delivery of protons, electrons, and gaseous CO_2 to the catalyst, maximizing mass transport.[145,146] Multiple porous cathode layers must be used to ensure control of reactant delivery rate, making these GDEs more complex than those for type 1 and type 3 electrolyzers. Catalyst placement within carbon layers can have a substantial impact on GDE performance.[128] These GDEs are typically produced by airbrushing inks containing a catalyst nanopowder and ionomer dispersion onto a carbon-based diffusion layer,[147] electrodeposition onto carbon paper,[148] incorporation into carbon-diffusive materials,[149] or roll-out methods using carbon pastes on metal mesh,[107] although in many cases leakage of the catholyte through the GDE is a hurdle for continuous operation.[150]

The key advantage of these room-temperature electrolyzers that use a gaseous CO_2 feed is their capability to sustain high current density, durability, product separability, and energy efficiency, all of which are key quantitative metrics for benchmarking. Use of practical CO_2 streams in an operational environment, however, calls for effective utilization of dilute waste CO_2. Changes in the gaseous cathode feed may adversely affect catalyst, membrane lifetime, and pH at the electrode surface but are underdeveloped.

Type 3: High-Temperature Electrolysis

Solid-oxide electrolyzers use gaseous inputs for both anode and cathode feeds by using porous and diffusive ceramic materials for both electrodes, with a solid

electrolyte for ion conduction at temperatures between 300°C and 1,500°C, and have seen substantial stand-alone and integrated product development as a result of their high reliability and long lifetime.[151,152] Their high-temperature operation reduces their utility for on-demand CO generation, and demonstrations of C_{2+} products from these systems are limited. For CO generation, they have high thermal efficiency and reliability when fed with a pure CO_2 input stream to the cathode. Their key drawbacks are susceptibility to system degradation caused by impurities in feedstock CO_2 and limited transient operation,[28] yet despite these shortcomings, this technology is approaching a commercial reality—a 12-kW demonstration system was reported in 2017.[153]

OUTLOOK

As the consequences of increasing CO_2 concentrations in the atmosphere become more severe, the adoption of large-scale carbon-negative technologies is necessary. Nature has shown us that water is a viable reagent and oxygen a benign by-product for CO_2 conversion on these scales. Of the methods for small-molecule synthesis from CO_2, water, and renewable energy, electrolysis can selectively produce various products on-site, in a single electrochemical step, using only electricity to power the process. Technology development must be directed toward leveraging these products in markets with relevant near-term pain points.

The variety of products and their potential for high-purity production with high selectivity is a unique value proposition for applied CO_2 electrolysis. To access these requirements, key hurdles in GDE design, which affect electrolyzer reliability and production rate, must be overcome. Care must be taken to avoid excessive energy use in a CO_2 electrolyzer, and system design should enable future improvements in energy efficiency. However, energy efficiency only becomes a market pain point after the prior barriers are traversed and fuel markets are being pursued. At present, approaches that emphasize reliability, durability, and production rate are most desirable.

Because they meet these requirements, CO_2 electrolyzers that utilize a gaseous CO_2 feed have potential for commercialization and global deployment. These systems can also leverage existing infrastructure and development that has taken place for PEM water electrolysis. Other techniques using aqueous and non-aqueous CO_2 capture solutions, which may yet overcome some of these developmental advantages, are arising. Further research is required to understand and develop methods to increase CO_2 concentration at active sites, turnover of adsorbed species, and product selectivity at high current densities. Applied research can implement this fundamental knowledge to design reactors that enable high throughput and leverage the potential for on-site production integrated with economic CO_2 sources.

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AUTHOR CONTRIBUTIONS

C.C., J.F.K.K., and S.W.S. analyzed the literature, investigated economic data, and wrote the manuscript. S.W.S. supervised the work.

DECLARATION OF INTERESTS

The authors have submitted patents on carbon dioxide conversion technologies, including patent applications PCT/US2017/056589, PCT/US2018/040442, and US16/012749. The authors are employees of Catalytic Innovations, which has a financial interest in these patents.

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